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Characterization of Chemically Synthesized Polyaniline-Zinc Oxide Nanocomposites

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ABSTRACT

In the present paper, pure nanocrystalline zinc oxide compound was synthesized by chemical co-precipitation method. The composite of Polyaniline with nanosized Zinc Oxide was prepared by In-situ chemical oxidation polymerization method with ammonium per sulphate as an oxidant in aqueous hydrochloric acid under constant stirring at 0-4 ^{0} C in presence of Nitrogen atmosphere. The d.c. electrical conductivities as a function of temperature (298-423 K) were measured by four probe technique. Electrical conductivity of composite with 20 % weight of Zinc Oxide is found to be more among all other composites and even than polyaniline. FTIR studies showed that there is strong interaction between polyaniline and nano sized Zinc Oxide particles.

Keywords: Polyaniline, nanosized Zinc Oxide, Nanocomposite, conductivity, FTIR**.**

INTRODUCTION

Recently nanocomposite materials have become one of the most extensively studied material all over the world as they have shown to possesses several technological application such as effective quantum electronic devices, magnetic recording materials sensors etc.[1]. Moreover nanocomposite material composed of conducting polymers & oxides have open more field of application such as drug delivery, conductive paints, rechargeable batteries, toners in photocopying, smart windows, etc [2, 3].

Conducting polymers provide tremendous scope for tuning of their electrical conductivity from semiconducting to metallic region by way of doping [4] and are organic electro chromic materials with chemically active surface. But they are chemically very sensitive and have poor mechanical properties and thus possessing a processibility problem. Nanomaterial shows the presence of more sites for surface reactivity, they possess good mechanical properties and good dispersant too [5]. Thus nanocomposites formed by combining conducting polymers & inorganic oxides nanoparticles, possess the good properties of both the constituents & thus enhanced their utility. The properties of such type of nanocomposite are strongly depending on concentration of nanomaterials to be added. Among the organic conducting polymers polyaniline (PAni) is the only conducting polymer whose properties not only depend on the oxidation state but also on it protonation state / doping level and also on the nature of dopants. It possesses excellent electric, magnetic and optical properties. It is generally regarded as one of the conducting polymer with high potential in commercial application.

Nanosized inorganic semiconductor materials have attracted considerable efforts in recent years zinc oxide is an interesting materials has been widely used in application such as UV protection, photo catalysis, filed emission displays, veristors, gas sensors, function devices, thermoelectric materials, etc [6] due to its exceptional physical & chemical properties. Conducting polymer nanocomposite of PAni and zinc oxide nanoparticles can exhibits some novel properties. In this paper nano crystalline zinc oxide was prepared by co-precipitation method, and then it's composite with PAni was prepared by in–situ chemical oxidative polymerization method and characterization by electrical conductivity and FTIR.

2. Experimental Details

All chemical used were of analytical grade, Aniline, ammonia solution (min 25%), zinc nitrate (96%), acetone, ethyl alcohol are from Merk Ltd, Mumbai and ammonium persulphate from SD fine chem., India were used as received without further purification. Double distilled water was used throughout this work. The sample of pure zinc oxide compound was prepared by co-precipitation method. The solution of 0.2M of zinc nitrate [$Zn(NO_3)_2 \, 6H_2O$] was prepared in distilled water and to this solution ammonia solution was added dropwise till the pH adjusted to 8. The hydrated zinc hydroxide get thus formed was thoroughly washed with distilled water and transfer to flask fitted with water condenser. The gel was continuously stirred for 6 Hours and temperature was maintained around 85^0 C. then, the crystalline powder was filtered and oven dried [8]

Polyaniline – ZnO nanocomposites were prepared for different wt of % (5%, 10%, 15%, 20%, and 25%) of ZnO by in-situ oxidation polymerization method. Initially known wt. of ZnO (5%) was added to aniline prepared in aqueous hydrochloric acid (1M) and stirred for half an hour, then allow settling down for another half an hour. To this solution, ammonium persulphate as an oxidant prepared in aqueous hydrochloric acid (1M) was added drop-wise for half an hour under constant stirring at 0–4^0C in presence of nitrogen atmosphere. The monomer to oxidizing agent ratio was kept at 1: 1.25. Stirring was continue for eight hours, the resulting dark green mixture was kept over night and then filter. The precipitated polymer was washed with distilled water until the filtrate was colorless, then with acetone and methanol to remove excess initiator, monomer and oligomer. Finally, the polymer was dried in air for about a day and then in an oven at 80^0C for 15 hours. Similarly nanocomposites for remaining wt % of ZnO were prepared. The nanocomposites with 5%, 10%, 15%, 20% and 25% wt of ZnO are named as PZ_1, PZ_2, PZ_3, PZ_4 and PZ_5 respectively.

The four probe set up model DFP-RM (SES Roorkee) was used to measure electrical conductivity of samples in pallet form, made using dye-punch of 1 cm diameter in a hydraulic press (scientific engineering corporation, India) under a pressure of 7 tons. The FTIR spectra of the nanocomposites were recorded in KBr by using "SHIMATZU MODEL – 810A FTIR" spectrophotometer between 400 and 4600 cm^{-1}

RESULTS AND DISCUSSION

3.1 Electrical conductivity

The in-situ oxidation polymerization method can be a general and useful procedure to prepare conductive polymer and its composites. It is well established that the charge transport properties of conjugated polymers strongly depend on the processing parameter [9]. Polyaniline has a reactive N-H group in a polymer chain flanked on either side by a phenylene ring, imparting a very high chemical flexibility. It undergoes protonation and deprotonation in addition to adsorption through nitrogen, which having lone pair of electrons, is responsible for the technologically interesting chemistry and physics.

The plot of surface d.c. conductivity of conducting PAni and its composite with temperature are shown in fig 1.It is observed that conductively is found to increase with increases in temperature. This increase in conductivity with temperature is the characteristic of "thermal activated behavior". The increase in conductivity could be due to increase of efficiency of charge transfer between the polymer chains and the dopant with increase in temperature [10]. It is also possible that the thermal curing affects the chain alignment of polymer, which leads to the increase of conjugation length and that, brings about increase in conductivity.

The conductivity of composites PZ_1 and PZ_4 are found to be more than pure PAni over the entire temperature range 300–423k and maximum for PZ_4. This increase in conductivity could possibly be explained on the basis of percolation theory [11]. Which predicts that at a certain amount of concentration of filter material a continuous full conducting path is formed for the flow of current give rise more conductivity than that pure PAni.

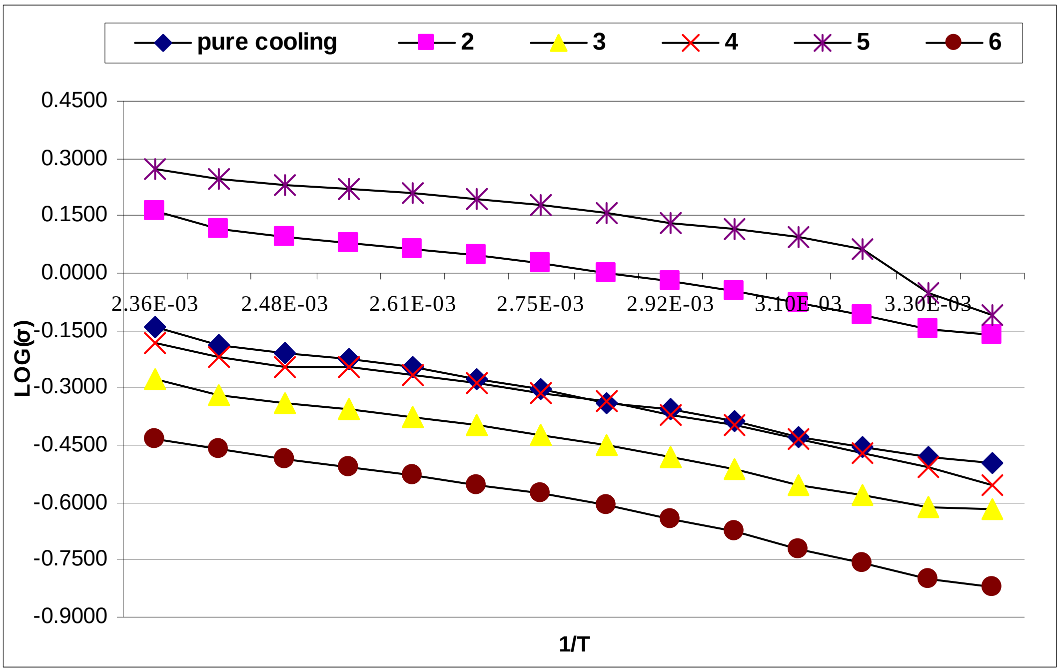

Fig1:Variation of electric conductivity with temperature.

3.2 Fourier transform infrared spectroscopy

The FTIR transmission spectra of pure materials and their composites were recorded in the range 400 – 4600 cm^{-1} to confirm polymerizations of PAni are shown in fig2.

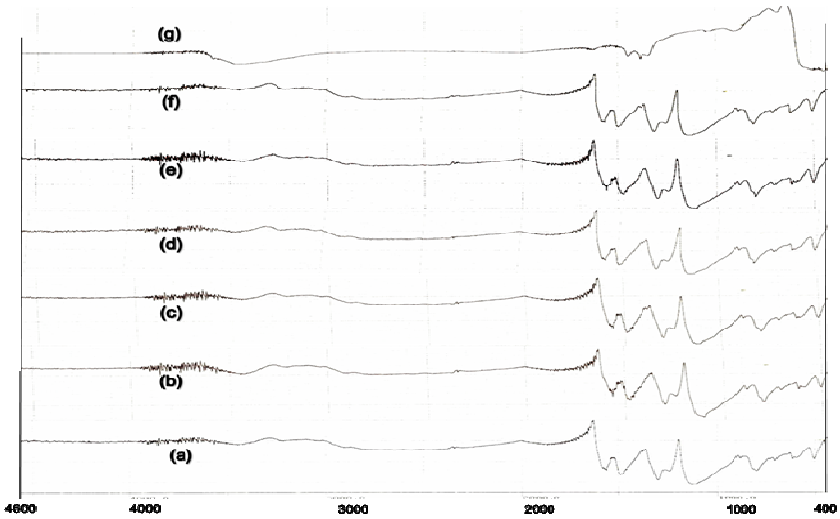

Fig: 2 FTIR Spectra (a) Pure PAni, (b) PZ1, (c)PZ2, (d) PZ3, (e) PZ4, (f) PZ5 and (g) Pure ZnO.

In fig. 2a peak at 3460 and 3230 cm^{-1} can be attributed to the free (non hydrogen bonded) N–H stretching vibration and hydrogen bonded N-H bond between amine and imine sites, C=N and C=C stretching modes for the quinonoid and benzenoid units occur at 1560 and 1498 cm^{-1}, the band at 1298 cm^{-1} has been attributed to C-N stretching mode for benzoid unit, while the strong band at 1128 cm^{-1} was considered to be a measure of the degree of electron delocalization and thus it is a characteristic peak of PAni. The peak at 800 cm^{-1} is due to the N-H out of plane bending absorption. The FTIR spectrum of ZnO (fig 2b) shows the presence of bands around 3477 cm^{-1} and 1560 cm^{-1} confirms the formation of pure ZnO compound. The band 3477 cm^{-1} corresponds to the stretching vibrations of the OH group on the surface of ZnO nanoparticles [12]. The FTIR spectra of composites (fig 2c-g) show that intensities of most of the peaks are affected by the presence of ZnO during polymerization of PAni. This can be explained on the basis of constrained growth and restricted modes of vibration in PAni grown in presence of ZnO. In this case the monomer gets absorbed on oxide particles and polymerization proceeds initially on the surface of the oxide particles when ammonium persulphate is added to the solution. This leads to the adhesion of the polymer to the ZnO particles. As a result the characteristics stretching frequencies are shifted towards higher wave number side, as compared to pure PAni. Thus there is strong interaction of ZnO with PAni. This is also confirmed from electrical conductivity studies.

CONCLUSION

Nanocomposites of PAni and Zinc oxide were synthesized by in-situ chemical oxidative polymerization technique using hydrochloric acid as a dopant. Temperature dependence surface conductivity shows that, conductivity of composite with 20% wt of ZnO is maximum among other composites and also more than that PAni. This may be due to formation of continuous full conduction path for the flow of current. FTIR studies also showed there exist strong interaction between PAni and Nanosized ZnO particles.

REFERENCE

[1] Anderson A, Hunderi O and Granqvist , *J. Appl. Phys*., **1980,** 57,75
[2] Jarjayes O, Fries P H and Bidan G ,*Synthetic metals* , **1995**, 69,343
[3] Butter worth M D, Corradi R, Johal J, Lascelles S F, Maeda S, and Armes S.P , *J Colloid Interface sci.*, **1995**, 174,510.
[4] Wessling B , Handbook of conducting polymers [New York, Marcel Dekker Inc Press] P, **1998**, 471
[5] Jewell J L, Harbison J P, and Scherrer A ,*Sci.Am*., **1991**,5, 265.
[6] Wang Z and Li H ,*J Appl. Phys.* A,**2002**,74, 201
[7] Tsuzuki T and Mccormick P. G *Scripta mater*, **2001**,44,1731
[8] Anbukumar S, Vasudevan S and Ramasamy P, *J Meter Sci. Lett*.,**1986**, 24 ,233
[9] CaO Y, Qiu J and Smith P, *Synth.. Met,* **1995** ,69,187
[10] Kobyashi A, Ishikawa H, Amano K and Satoh M, *J. Apply Phys*.,**1993**74, 296
[11] Suri Komilla, Annapoorni S, and Tandop R P ,*Bull Mater Sci*., **2001** , 24, No. 6, 563-567
[12] Vaezi M R, *Materials and Design*, **2007**,28,1065